



Thermal stabilization and decomposition of simple glycosides in the presence of aromatic substances in closed ampoules: The role of $\text{OH} \cdots \pi$ hydrogen bonding

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ABSTRACT

The thermal reactivities of some simple glycosides (methyl α - and β -D-glucopyranosides, methyl β -D-xylopyranoside and levoglucosan (1,6-anhydro- β -D-glucopyranose)) in aromatic substances were studied in closed ampoules. Under neat (molten) conditions (N_2 , 15 min), these glycosides decomposed completely over the temperature range 260–280 °C. These same compounds, however, were stable in diphenyl ether up to approximately 320–340 °C. The ^1H NMR signals assigned to the C–Hs of the glycosides shifted to higher magnetic fields on addition of guaiacol (2-methoxyphenol) to their D_2O solutions, suggesting $\text{CH} \cdots \pi$ interactions occur between the glycosides and guaiacol. A red shift of the IR signals assigned to the stretching of $-\text{OH}$ groups of the glycosides was observed in aromatic solvents, indicating $-\text{OH} \cdots \pi$ hydrogen bonding. These results are explained by a mechanism similar to that proposed for interactions with polyethers; the formation of $-\text{OH} \cdots \pi$ hydrogen bonding inhibits proton donation to the oxygen atoms of the glycosides, thus inhibiting acid-catalyzed pyrolysis reactions. At temperatures above 350 °C these glycosides degraded even in aromatic solvent but with different pathways. Char, water and furanic compounds (common dehydration products) were not produced, whereas CO , CO_2 and low molecular weight aliphatics were selectively generated. Interestingly, these reactions exhibited zero-order kinetics. These observations can be explained by thermal decomposition in the gas phase following evaporation of the glycosides.

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1. Introduction

Pyrolysis is the most fundamental aspect of a number of thermochemical conversion techniques applied to biomass resources, including fast pyrolysis, gasification, carbonization and torrefaction. Improving the product selectivity of such processes is challenging but is a necessary prerequisite to allowing for the practical application of these techniques to the production of biofuels, biomaterials and biochemicals from biomass. Accordingly, a better understanding of the molecular mechanisms of biomass pyrolysis is important.

Carbohydrates such as cellulose, hemicellulose and starch often represent the major chemical components of biomass. Pyrolysis of simple glycosides starts with the cleavage of the glycosidic bond, known as transglycosylation, and this is normally observed around

200–300 °C [1–4]. Various subsequent reactions may follow this initial step, including polymerization, dehydration and fragmentation [5]. These assorted pyrolytic reactions eventually result in the formation of a complex mixture of products [5].

Hosoya et al. [6] found that this sequence of reactions varies in the presence of certain aromatic substances. Levoglucosan (1,6-anhydro- β -D-glucopyranose), the important primary pyrolysis product from glucose-based carbohydrates, was observed to be stable up to 340 °C when heated as a solution in various aromatic compounds. Hosoya's work determined that the effectiveness of an aromatic in this regard is directly related to the π -electron density of the benzene ring. Complexation of levoglucosan with aromatic substances through $\text{CH} \cdots \pi$ interactions has been suggested by changes in the ^1H NMR spectra of levoglucosan in D_2O upon the addition of increasing amount of guaiacol (2-methoxyphenol). The stabilization mechanism, however, has not yet been properly understood.

Similar stabilization of reducing sugars [7] and glycosides [8] in polyethers has been reported. Matsuo et al. [7] found that glucose, a reducing sugar, was stabilized in polyethers, including

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tetraethyleneglycol dimethyl ether. Fragmentation products such as glycolaldehyde, 1,3-dihydroxyacetone and formaldehyde were formed selectively (maximum yield: 74.9 wt%) at temperatures above 220 °C, a temperature that is slightly higher than the temperature usually applied during the pyrolysis of molten glucose. Based on these results, they proposed a stabilization mechanism which includes hydrogen bond formation between the sugar hydroxyl groups –OH (as proton donors) and polyether oxygens (as proton acceptors). This bonding inhibits proton donation to the oxygen atoms of the sugar through intermolecular hydrogen bonding between sugar molecules. Such hydrogen bond formation between the hydroxyl groups of glycosides and ether oxygens has been deduced from analysis of IR spectral peaks assigned to the stretching mode of the –OH groups of glycosides [8].

For this reason, proton donation through intermolecular hydrogen bonding is expected to act in the same manner as an acid catalyst to promote transglycosylation and dehydration as the primary pyrolysis reactions of sugars and glycosides. Considering this acid catalysis mechanism, the earlier observations are reasonably explained by assuming that the decomposition pathway of the levoglucosan changes in the gas phase such that gaseous products (CO and CO₂) are formed selectively [9]. The π electrons of aromatic substances are also expected to act as acceptors for hydrogen bonding by –OH groups of glycosides [10–14], as in the case of ether oxygens. This, however, has not yet been confirmed.

In this work, the thermal reactivities of some simple glycosides (methyl α - and β -D-glucopyranosides, methyl β -D-xylopyranoside and levoglucosan) in closed ampoules in the presence of aromatic compounds were studied and contrasted with the results of pyrolysis under neat (molten) conditions. Interactions between the glycosides and the aromatics were characterized based on ¹H NMR and IR spectra. Furthermore, the effects of increasing pyrolysis temperatures on the thermal decomposition pathways of these glycosides when combined with aromatics in closed ampoule reactors were also investigated.

2. Experimental

2.1. Materials

Methyl β -D-glucopyranoside (**1**), methyl α -D-glucopyranoside (**2**) and levoglucosan (**4**) (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) and methyl β -D-xylopyranoside (**3**) (Nacalai Tesque Inc., Kyoto, Japan) were used without further purification. Diphenyl ether (DPE), 1,3,5-triphenylbenzene and phenanthrene were purchased from Tokyo Chemical Industry Co. Ltd., Tokyo, Japan. Other solvents and chemicals were obtained from Nacalai Tesque Inc., Kyoto, Japan.

2.2. Heat-treatment in closed ampoules

Glycoside or levoglucosan (4 mg) and DPE (100 μ L) were placed at the bottom of a Pyrex glass ampoule (internal diameter: 2.0 mm, thickness: 1.0 mm). The glass ampoule was closed (final length: about 30 mm) after exchanging the inside air with N₂ by using an aspirator. The ampoule was heated for 1.5–60 min in an upright setting by inserting the ampoule into a muffle furnace preheated at 280–420 °C through a small hole at the top. The pressure inside the ampoule was atmospheric pressure before pyrolysis and increased during the pyrolysis, although the pressure was not monitored in this study. After pyrolysis, the ampoule was immediately cooled by flowing air for 1 min and opened. When the product gas was collected for analysis, the ampoule was opened with the gas collecting apparatus attached to the ampoule according to the previous paper [9]. The non-condensable gases were analyzed by gas

chromatography (GC) as described later. Then, the ampoule was extracted with dimethyl sulfoxide (DMSO)-*d*₆ (1.0 mL) to obtain the DMSO-*d*₆-soluble fraction. Heat-treatment under neat (molten) conditions was also conducted without addition of any aromatic substances.

Recoveries of the glycosides and levoglucosan were determined based on the signals assigned to the C1-protons of the ¹H NMR spectra, which were obtained for the DMSO-*d*₆-soluble fractions with a Bruker AC-400 (400 MHz) spectrometer, using an internal standard (phloroglucinol). MeOH, acetic acid, formic acid, hydroxyacetone, furfural, 5-hydroxymethylfurfural (5-HMF) were quantified based on the signals at δ 3.2 (CH₃), 1.9 (CH₃), 8.3 (aldehyde-H), 2.0 (CH₃), 9.6 (aldehyde-H) and 9.7 ppm (aldehyde-H), respectively. Yield of water was determined by the peak area of the signal at 3.4 ppm compared with that of pure solvent.

The gaseous products were analyzed by GC on a Shimadzu GC-18B after the addition of 0.5 mL of neon (an internal standard). The chromatographic conditions were column: Shincarbon ST (4.0 m $\times$ 3.0 mm ϕ), carrier gas: Ar, flow rate: 20 mL/min, column temperature: 40 °C (0–1 min), 40–200 °C (1–21 min, 8 °C/min), 200 °C (21–31 min); detector: thermal conductivity detector (TCD); retention times: H₂ (3.8 min), N₂ (9.6 min), CO (11.2 min), CH₄ (16.8 min) and CO₂ (22.6 min).

Heat-treatment experiments were repeated several times for all conditions, and we confirmed that the obtained results were not so different with each other.

2.3. NMR measurement

Glycoside (10 μ mol) was dissolved in D₂O (1.0 mL) including 1.2–18.6 mg (10–150 μ mol) of guaiacol. After ultrasonic wave treatment for 10 min, the solution was used for ¹H NMR analysis at 24 °C.

2.4. IR measurement

IR spectra were recorded in transmission mode with a Nicolet Continuum infrared microscope (Thermo Fischer Scientific Inc., Waltham, MA, USA) attached to a Nicolet iS10 FT-IR spectrometer (Thermo Fischer Scientific Inc., Waltham, MA, USA) using a heating stage (Model S100, S.T. Japan Inc.) with a thermal controller (KP1000C, CHINO Corporation). Levoglucosan or glycoside and aromatic substances were mixed together with a mortar and placed between two BaF₂ windows (diameter: 13 mm, thickness: 1.0 mm) and set into the heating stage. Measurements were conducted under a nitrogen flow (10 mL/min).

3. Results and discussion

3.1. Stabilization in aromatic substances

The recoveries of methyl glycosides (**1–3**) and levoglucosan (**4**) after 15 min of pyrolysis in DPE under N₂ in closed ampoules are summarized in Fig. 1. The results obtained following neat pyrolysis under N₂ in closed ampoules are also included for comparison purposes. All four compounds evidently began to decompose around 200–260 °C and were completely degraded when the samples were heated at 280 °C. The reactivities of these compounds varied, however, depending on their chemical structures, in the following order: **3**, **4** > **2** > **1**. In contrast, these same compounds in DPE were stable up to approximately 320 °C. These results are in good agreement with our earlier observations during trials with levoglucosan [6] and confirm the stabilization effects of aromatic substances also apply to methyl glycosides.

Fig. 2 shows the changes in the chemical shifts ($\Delta\delta$) of the ¹H NMR signals assigned to the C–Hs of the pyranose rings of

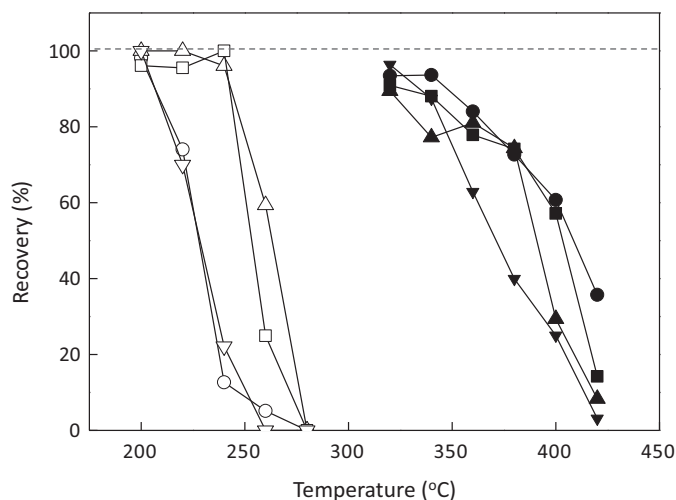


Fig. 1. Recoveries of methyl glycosides (**1–3**) and levoglucosan (**4**) following 15 min pyrolysis in diphenyl ether (DPE) under N_2 in closed ampoules at various temperatures. Levoglucosan (**4**) (○), methyl α -D-glucopyranoside (**2**) (Δ), methyl β -D-glucopyranoside (**1**) ($\square$), methyl β -D-xylopyranoside (**3**) (∇). Empty symbols: under N_2 , filled symbols: in DPE.

compounds **1–3** following the addition of increasing amounts of guaiacol to their D_2O solutions. The shift to higher magnetic fields observed in the case of some signals can be attributed to the shielding effect of aromatic π electrons, due to hydrogen bonding of the glycoside C–Hs with the benzene ring of guaiacol. Accordingly, $CH\cdots\pi$ interactions could be inferred from these changes in the chemical shifts. Geometries of the complexes that compounds **1–3** form with the aromatic ring of guaiacol are also shown in Fig. 2, which were optimized at the DFT (M06-2X) level, where the 6-31G(d), 6-31+G(d), 6-31G(d,p), and 6-31G basis sets were employed for C, O, H of the glycosyl moiety, and H of the aglycone,

respectively. These results also support the formation of $CH\cdots\pi$ hydrogen bonds. The lower $\Delta\delta$ values observed for methyl α -D-glucopyranoside (**2**) may arise from less effective complexation between **2** and guaiacol in this $CH\cdots\pi$ interaction mode, since the axial orientation of the methoxy group of **2** may inhibit interaction with the aromatic ring due to steric hindrance.

Infrared spectra (IR) over the range $3000\text{--}4000\text{ cm}^{-1}$, a region assigned to the stretching of hydroxyl groups, are useful for understanding the hydrogen bonds formed in sugars and glycosides [15,16]. Using this method, Kawamoto et al. [8] analyzed the hydrogen bonding between levoglucosan and tetraethyleneglycol dimethyl ether, a polyether, in which the $-OH$ groups of levoglucosan act as hydrogen bond donors to the ether oxygens (which are hydrogen bond acceptors). A similar procedure was applied for the analysis of hydrogen bonding in the mixtures of levoglucosan and glycosides with aromatic substances in this study, and provided information that could not be obtained by NMR analysis in D_2O .

The $-OH$ stretching regions of the IR spectra are shown in Fig. 3, acquired over the temperature range $20\text{--}240^\circ\text{C}$ for pure levoglucosan [8] and a mixture of levoglucosan and 1,3,5-triphenylbenzene (1:1 mol/mol). To investigate the role of aromatic π electrons, triphenylbenzene was used additionally, since DPE includes an oxygen atom which can act as a hydrogen bond acceptor. Hydrogen bonding may be depicted as $X-H\cdots Y-Z$, and the length of the $X-H$ bond usually increases on the formation of hydrogen bonds, leading to a red shift in the $X-H$ stretching frequency as well as increases in the absorption intensity [17,18]. The $-OH$ stretching bands of alcohols are normally observed in three regions: $3600\text{--}3650$, $3450\text{--}3600$ and $3250\text{--}3450\text{ cm}^{-1}$, which are assigned to free $-OH$ and intra- and intermolecular hydrogen bonds, respectively [19]. The red shift associated with intermolecular hydrogen bonds is caused when $-OH$ acts as both hydrogen bond donor and acceptor. As discussed in our previous paper [8], the very broad signals observed for pure levoglucosan at 150 and

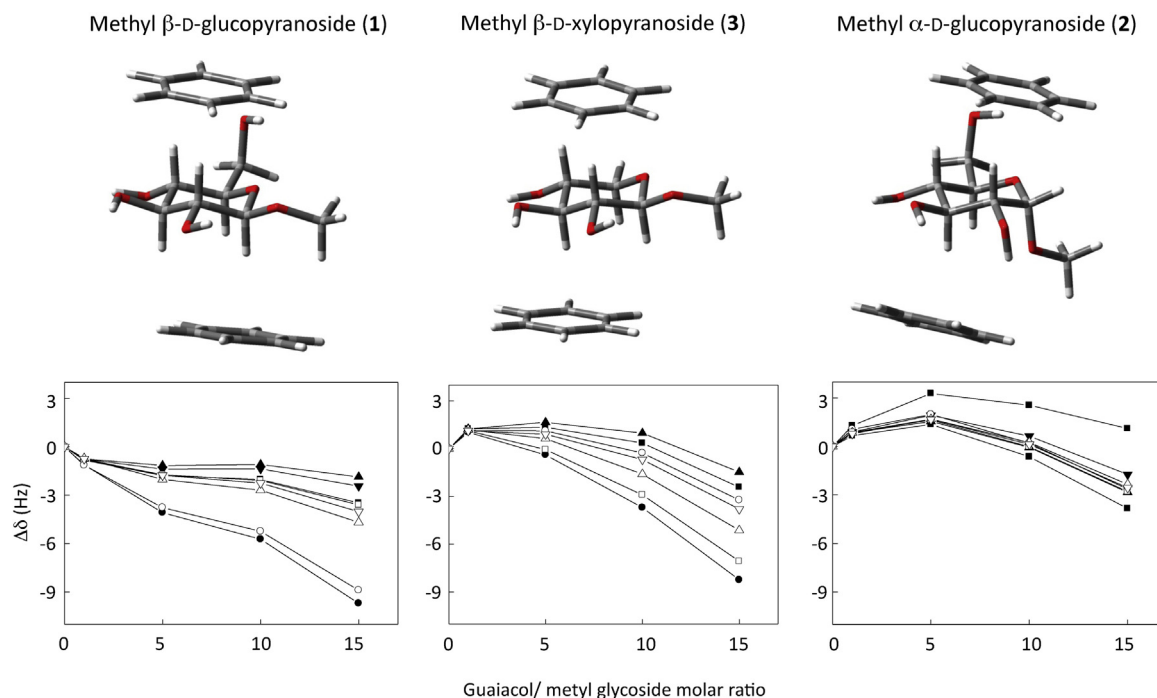


Fig. 2. Changes in the chemical shifts of the ^1H NMR signals assigned to the C–Hs of the pyranose rings of compounds **1–3** by the addition of increasing amounts of guaiacol to the D_2O solutions, along with the geometries of the complexes optimized at the DFT (M06-2X) level. $C_1\text{--}H$ (○), $C_2\text{--}H$ (Δ), $C_3\text{--}H$ ($\square$), $C_4\text{--}H$ (∇), $C_5\text{--}H$ (●), $C_5\text{--}H$ (for **3**) (◆), $C_6\text{--}H$ (▲), $C_6\text{--}H$ (■), methyl- H (▼). The 6-31G(d), 6-31+G(d), 6-31G(d,p), and 6-31G basis sets were employed for C, O, H of the glycosyl moiety, and H of the aglycone, respectively.

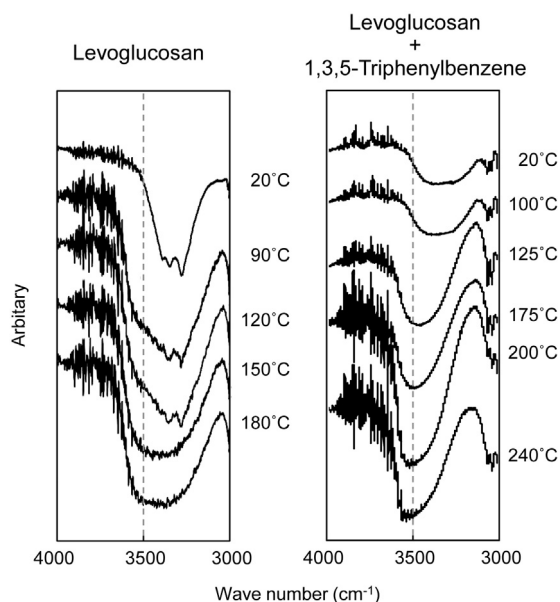


Fig. 3. Changes in the OH stretching region at elevated temperatures in the IR spectra of pure levoglucosan and levoglucosan with 1,3,5-triphenylbenzene (1:1 mol/mol).

190 °C indicate the involvement of numerous types of structure including intermolecular hydrogen bonds, even at such high temperatures.

In contrast, the relative intensities of the signals in the range of 3250–3450 cm^{-1} decreased in 1,3,5-triphenylbenzene at temperatures above 125 °C, at which point the levoglucosan was dissolved. Similar results were obtained with other aromatic substances such as DPE and phenanthrene. These results show the suppression of the intermolecular hydrogen bonding between levoglucosan molecules. Since 1,3,5-triphenylbenzene has only π electrons which can act as hydrogen bond acceptors, these observations would arise from the formation of $\text{OH} \cdots \pi$ hydrogen bonds between aromatic π electrons and levoglucosan –OHs, as illustrated in Fig. 4A.

As proposed in the case of the polyether [7,8], these hydrogen bonds between the levoglucosan/glycoside and the aromatic compound would inhibit proton donation to the oxygens of the levoglucosan/glycoside, which normally act as acid catalysts for transglycosylation and char-forming dehydration reactions. Under

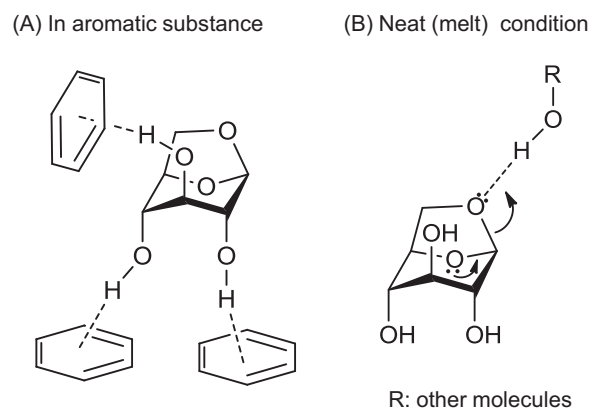


Fig. 4. Proposed structures for (A) the formation of $\text{O–H} \cdots \pi$ hydrogen bonds from levoglucosan in an aromatic solvent and (B) the acid-catalyzed transglycosylation by proton donation to the C_1 –oxygen through intermolecular hydrogen bond formation during the pyrolysis of molten levoglucosan.

neat (molten) conditions, such acid catalysis is possible through intermolecular hydrogen bonding between levoglucosan/glycoside molecules, as illustrated in Fig. 4B.

The role of hydrogen bonding in carbohydrate pyrolysis has also been proposed based on theoretical calculations [20–23]. Hosoya et al. [20] have indicated that a bimolecular pathway including the participation of the –OH groups of other molecules makes the transformation from methyl β -D-glucopyranoside with a $^1\text{C}_4$ conformation to levoglucosan easier through lowering the associated activation energy. A similar bimolecular ionic mechanism, i.e., a concerted mechanism, was reported for the pyrolysis of glucose [21] and cellulose [22,23] based on similar theoretical calculations.

3.2. Decomposition in the presence of aromatic substances

As shown in Fig. 1, compounds 1–4 degraded even in DPE at temperatures above approximately 350 °C. Fig. 5 presents a photograph of the reaction mixture after pyrolysis of methyl β -D-glucopyranoside (1) in DPE in a closed ampoule at 420 °C for 15 min, along with the ^1H NMR spectrum of a DMSO- d_6 solution of the resulting pyrolysis mixture, including the DPE. The pyrolysis mixture retained a light brownish-yellow color even at such high temperatures, and no solid carbonized products were observed. In the NMR spectrum, signals assigned to levoglucosan, MeOH, hydroxyacetone and acetic acid were observed along with other

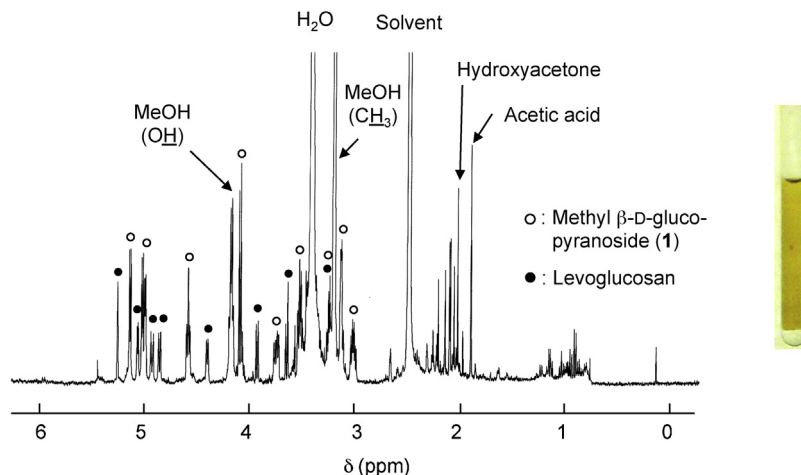


Fig. 5. Photograph of the reaction mixture obtained after pyrolysis of methyl β -D-glucopyranoside (1) in DPE at 420 °C for 15 min in a closed ampoule along with the ^1H NMR spectrum of the reaction mixture (including DPE) in DMSO- d_6 solution.

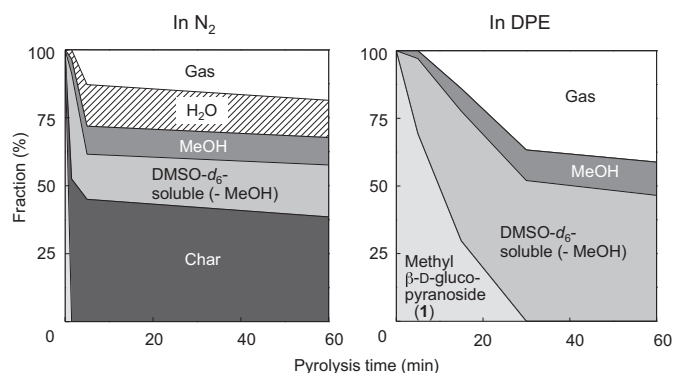


Fig. 6. Changes in the product composition during pyrolysis of methyl β -D-glucopyranoside (**1**) in DPE at 420 °C, compared with the results obtained in N_2 .

signals, including those of unreacted **1**. Many signals were also observed in the chemical shift range of 0.8–1.2 and 2–2.5 ppm. These signals may be assigned to aliphatic methyl and methylene protons of carbonyl compounds, indicating that large numbers of unknown aliphatic carbonyl compounds were formed during the pyrolysis in DPE, although more detailed identification of these products was not conducted. MeOH would be formed from the aglycone moiety of **1**, which indicates cleavage of the glycosidic bond during pyrolysis. A signal due to water was observed as a contaminant in the DMSO- d_6 .

Changes in the product composition obtained from compound **1** during pyrolysis in DPE at 420 °C are summarized in Fig. 6, compared with the results obtained under N_2 . Yields of gases and low MW products determined in the DMSO- d_6 -soluble portions for some selected pyrolysis conditions are presented in Table 1. Pyrolytic decomposition of **1** evidently proceeded much faster under N_2 than in DPE at 420 °C, and the product compositions varied greatly between these two conditions; **1** was converted to char and water along with MeOH very quickly, indicating char-forming dehydration and transglycosylation reactions were predominant during pyrolysis in N_2 . The yield of MeOH (14 wt%) following 5 min pyrolysis corresponds to approximately 90% of the theoretical yield (16 wt%) from the aglycone portion of **1**. Levoglucosan, furanic compounds such as 5-HMF and furfural, hydroxyacetone, acetic acid and formic acid (Table 1) were also detected as low MW products in the DMSO- d_6 -soluble portion obtained from the early stage of pyrolysis (1.5 min). All these results are expected based on the typical pyrolysis reactions reported for glycosides and other carbohydrates [5].

In contrast, compound **1** decomposed much more slowly in DPE and was not converted to char and water. Furfural and 5-HMF were also not detected, both of which are dehydration products. These observations suggest that dehydration reactions were completely inhibited in DPE, although dehydration is the most characteristic reaction in the pyrolysis of glycosides and other carbohydrates. Instead of the formation of these products, non-condensable gases, including CO and CO_2 and the DMSO- d_6 -soluble low MW products were the major products in DPE (Table 1). Levoglucosan,

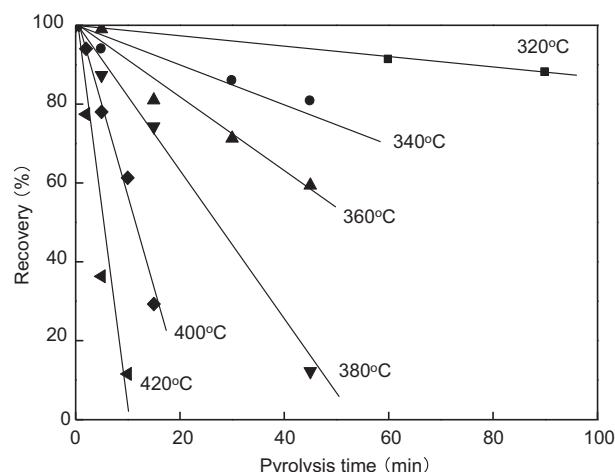


Fig. 7. Changes in the recovery of methyl α -D-glucopyranoside (**2**) during the pyrolysis in the presence of DPE in a closed ampoule at 320–420 °C.

hydroxyacetone and acetic acid were found in the DMSO- d_6 -soluble portions, along with the unidentified aliphatic compounds noted earlier. These product compositions are rather similar to those reported for the gas phase pyrolysis of levoglucosan in a closed ampoule [9].

Fig. 7 shows the changes in the recovery of methyl α -D-glucopyranoside (**2**) during pyrolysis in DPE in a closed ampoule over the temperature range 320–420 °C. Relationships between the amount of recovered **2** and the pyrolysis time tend to exhibit rather linear relationships even under the high conversion conditions of 380, 400 and 420 °C. Thus, it was surprising that the pyrolytic decomposition of **2** exhibited a close correspondence with zero-order kinetics. An Arrhenius plot of the decomposition rates of **2**, as calculated from the data of Fig. 7, is shown in Fig. 8. An activation energy, E_a of 32.9 kcal/mol was obtained for this conversion.

Zero-order kinetics and product compositions similar to those of gas phase pyrolysis may be explained with the proposed decomposition mechanism illustrated in Fig. 9, in which glycosides and levoglucosan decompose in the gas phase. Methyl glycoside or levoglucosan are stabilized when dissolved in aromatic substances through complexation associated with specific hydrogen bonding with aromatic π electrons. Accordingly, the methyl glycoside or levoglucosan evaporate and then decompose in the gas phase before undergoing the usual pyrolytic reactions including transglycosylation and char-forming dehydration. In this mechanism, the concentration of the methyl glycoside or levoglucosan would remain constant depending on the temperature/pressure conditions; decomposition in the gas phase would promote evaporation since the gas phase methyl glycoside or levoglucosan would exist in equilibrium with that in solution.

Based on the deuterium isotope effect of the addition of acetaldehyde on the decomposition reactivity of levoglucosan, Hosoya et al. [9] suggested the radical chain reactions involved in the gas-phase decomposition of levoglucosan in a closed ampoule.

Table 1

Yields (wt%) of gaseous and other low MW products from methyl β -D-glucopyranoside (**1**) at 420 °C.

Conditions	Recovery	Gas			Low MW products					
		CO	CO_2	CH_4	Levo glucosan	5-HMF	Furfural	Hydroxy acetone	Acetic acid	Formic acid
DPE/420 °C/15 min	29.7	9.1	4.5	0.29	5.9	ND	ND	1.5	0.73	ND
DPE/420 °C/60 min	ND	20.7	18.9	1.8	2.4	ND	ND	1.8	1.0	ND
N_2 /420 °C/1.5 min	ND	Trace	Trace	ND	1.2	0.22	0.24	0.14	0.10	Trace
N_2 /420 °C/60 min	ND	4.8	13.2	0.40	ND	ND	ND	0.31	0.54	ND

ND: not detected.

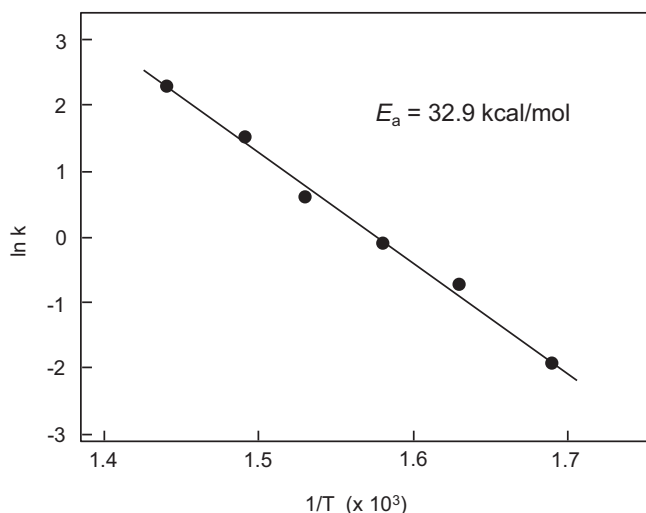


Fig. 8. Arrhenius plot for the degradation rates of methyl α -D-glucopyranoside (2) in the presence of DPE in closed ampoules at 320–420 °C.

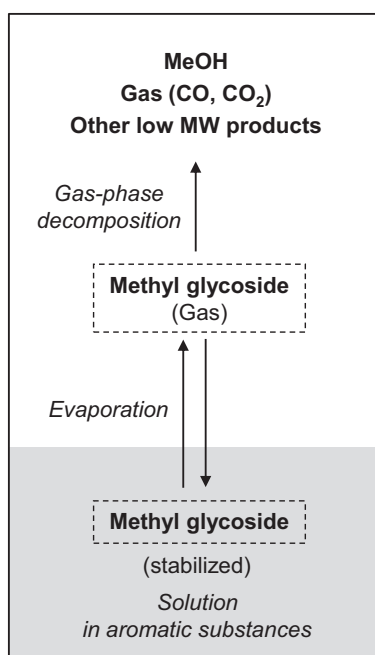


Fig. 9. Proposed mechanism for the decomposition of methyl glycoside in the presence of aromatic substances during pyrolysis in a closed ampoule.

The enthalpy of activation $\Delta H^\ddagger$, entropy of activation $\Delta S^\ddagger$, and Gibbs free energy of activation $\Delta G^\ddagger$ for the decomposition of **2** with DPE in a closed ampoule at 420 °C, which were calculated from the data of Fig. 7, were 30.1 kcal/mol, -13.6 cal/mol K, and 44.2 kcal/mol, respectively. Since pressure measurement inside the ampoule is not possible, these activation parameters were determined under the assumption that pressure in the ampoule remains constant during the pyrolysis experiment. The largely negative $\Delta S^\ddagger$ suggests that the decomposition of **2** proceeds in the mechanism other than the unimolecular decomposition mode. These results

also support the earlier proposal [9] which is based on the bimolecular type radical chain reactions. In the solution with aromatic compound, these radical chain reactions may be inhibited due to the “cage effect” arising from the solvation.

4. Conclusions

1. Simple methyl glycosides were stabilized at high temperatures when dissolved in aromatic substances.
2. $\text{CH}\cdots\pi$ and $-\text{OH}\cdots\pi$ interactions were suggested between methyl glycosides and aromatic substances.
3. The stabilization effect was explained based on the inhibition of the proton donation to glycoside oxygens through $-\text{OH}\cdots\pi$ hydrogen bond formation between the glycoside and the aromatic compound.
4. Methyl glycosides and levoglucosan decomposed in closed ampoules even in aromatic solvents at temperatures above 350 °C. The formation of char, water and furanic compounds was effectively inhibited, while the major products were CO, CO₂ and low molecular weight products such as levoglucosan (from glycosides) and aliphatic compounds.
5. Zero-order kinetics was observed for the decomposition of glycosides in closed ampoules in the presence of aromatic substances. Evaporation followed by gas phase decomposition was proposed for the reaction mechanism.

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